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OVERVIEW OF ACID HYDROLYSIS OF LIGNOCELLULOSICS TO LIQUID FUELS

John D. Wright and Charles E. Wyman
Solar Energy Research Institute
Golden, Colorado 80401

ABSTRACT

In this paper, an overview is presented of acid hydrolysis processes for conversion of lignocellulosic biomass into ethanol. First, biomass composition and acid hydrolysis kinetics are briefly reviewed to establish the limitations on acid catalyzed breakdown of cellulose and hemicellulose. Then, process descriptions are summarized for six acid catalyzed processes: The plug flow reactor, the percolation reactor, the progressing batch reactor, the low temperature concentrated sulfuric acid process, liquid phase hydrochloric acid hydrolysis, and liquid phase hydrofluoric acid hydrolysis. A summary of the economics of each option are presented along with projections of cost improvements that may be possible. Based on these considerations and the need to focus R&D on a few, promising options, the plug flow and progressing batch dilute acid hydrolysis processes are selected for engineering research at SERI, while the Tennessee Valley Authority (TVA) is pursuing the concentrated sulfuric acid hydrolysis process.

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INTRODUCTION

Cellulose, the major component of plants, is a polymer of glucose, which can be readily fermented to ethanol. If an inexpensive and efficient method can be developed for breaking down cellulose to sugar, it should be possible to design an economically attractive process for producing fuel ethanol from cellulosic materials. In this portion of the research review, the focus will be on acid hydrolysis-catalyzed processes for transformation of renewable lignocellulosic feedstocks into liquid fuels, octane enhancers, or fuel extenders. As in the rest of the program, liquid fuels are of interest because they are in short supply in this country and about half of our liquid fuels are imported, making the U.S. vulnerable to supply and/or price disruption in the future. Furthermore, liquid fuels command relatively high prices compared to solid or gaseous fuels, with gasoline at $1.00/gallon worth about $8.00/per million Btu. On the other hand, solid lignocellulosic substrates such as wood, agricultural residues, and municipal solid wastes, are limited in price to their energy equivalent of coal, about $2.00 per million Btu. Thus, the significant difference between the value of the solid biomass substrate and the price that can be demanded for liquid fuels that can be derived from this complex substrate could cover the conversion costs provided efficient use is made of the feedstock.

Either enzyme or acid catalyzed processes can be employed to break down the cellulose in biomass to form sugars that can be fermented into ethanol. Although enzymes ultimately promise to achieve very high yields of ethanol at low price, considerable research is still required to advance the technology to the point that it will be cost competitive. On the other hand, acid catalyzed hydrolysis of biomass can provide a near-term alternative to current starch-based technology because the technology has a long history of development. However, this advantage is offset by low yields for dilute acid processes, and high costs related to the consumption or recovery of acid in the concentrated acid process.

Feedstock Characteristics

Before discussing the acid hydrolysis options for cellulose conversion, it is useful to review some relevant aspects of lignocellulose chemistry. The carbohydrate portions of lignocellulose (crystalline cellulose, amorphous cellulose, and hemicellulose) can be hydrolyzed into their component sugars. Cellulose is a linear polymer of D-glucose (a six carbon sugar) molecules held together by beta-glycosidic bonds. Cellulose fibers are arranged in bundles of parallel chains in which adjacent chains are held together by hydrogen bonding between hydroxyl groups and hydrogen atoms, forming a crystalline material with great mechanical strength and high chemical stability. Because the bond between the glucose units is the weak link in the chain, the polymer can be broken (hydrolyzed) into its component sugars.

Hemicellulose is a polymer comprised primarily of five carbon sugars

(pentosans or xylans), six carbon sugars, and organic acids. The six carbon sugars are readily fermentable to ethanol, but standard industrial yeasts can not ferment the five carbon sugars. Unlike cellulose, the structure and composition of hemicellulose may vary widely between species. Hemicellulose is not crystalline and is readily hydrolyzed.

Lignin, the non-carbohydrate portion of the cell wall, is chemically bonded to, and mixed with, the hemicellulose. Lignin is a phenolic polymer and can not be converted to fermentable sugars (Wenzl 1970).

Theory of the Acid Hydrolysis of Cellulose

By understanding the mechanism of cellulose hydrolysis, it is possible to understand the rates and yields obtained via concentrated or dilute acid hydrolysis. To illustrate the hydrolysis mechanism, we will look at the hydrolysis of methylglucoside (Harris 1975, Goldstein 1983) (Figure 1). The analogy to cellulose hydrolysis is readily apparent if one envisions a string of glucose units attached by glycosidic bonds. For example, a second glucose unit would be attached where the methyl group is shown. In the proposed hydrolysis mechanism, the glycosidic oxygen is quickly protonated. The slow, rate-limiting step is the flexure of the glucose molecule from the chair configuration to the semiplanar configuration. This change in configuration is accompanied by the elimination of the methyl group from the glucose unit, and the next step is the rapid addition of water to the reactive end. The final step, also fast, is the regeneration of the catalytic proton from the newly formed glucose molecule.

It is generally accepted that the rotational energy required in the ring flexure is the rate-controlling factor in hydrolysis. The slow hydrolysis rates observed for crystalline cellulose is explained by the rigidity of the glucose rings held tightly in the crystal structure. Because cellulose chains are bonded to adjacent chains by hydrogen bonding between hydroxyl groups and hydrogen atoms, the close proximity and rigidity of the adjacent chains hinders the flexure of the glucose rings during hydrolysis. Since the ring flexure is the rate-determining step, the hindrance of adjacent chains decreases the hydrolysis rate. On the other hand, the hydrolysis rates of sugars in aqueous solution and the hydrolysis rate of solid hemicellulose sugars are much faster because their amorphous nature does not hinder the flexure of the ring.

One method of breaking down the chemically resistant crystalline cellulose is with high temperature dilute sulfuric acid. The major reactions of cellulose and hemicellulose degradation are shown below (Harris et al 1985):

Crystalline Cellulose ---> Glucose ---> HMF ---> Tars

Amorphous Cellulose ---> Glucose ---> HMF ---> Tars

Amorphous Xylan ---> Xylose ---> Furfural ---> Tars

Unfortunately, conditions severe enough to break down the crystalline cellulose are also sufficiently severe to degrade the product sugars. Therefore, sugar degradation is the central problem of dilute acid hydrolysis.
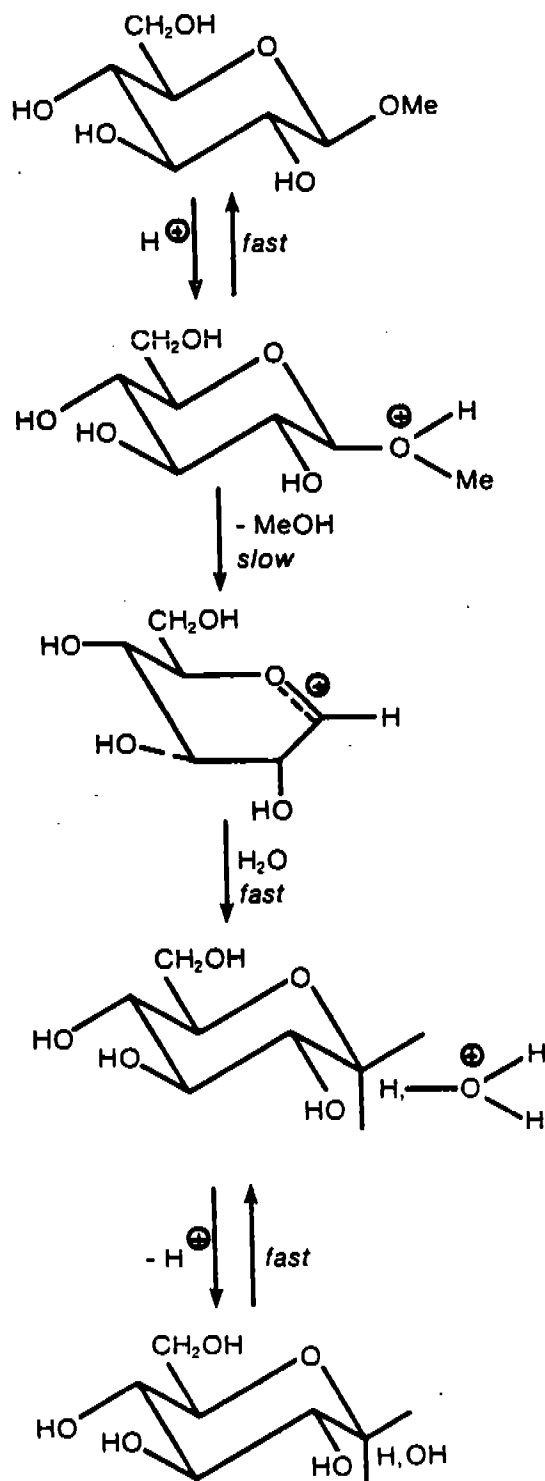
Figure 1.   Hydrolysis via the Cyclic Carbonium-Oxide Ion.

Because there is no structure to resist flexure of the sugar ring and slow the hydrolysis reaction, the hydrolysis of the amorphous cellulose and xylan can be carried out at low temperatures and acid concentrations (150°C and 1% H_2SO_4) where the conditions are not severe enough to significantly degrade either the sugars or the crystalline cellulose. This process is called prehydrolysis, and yields of greater than 80% can be achieved on the amorphous components. At 180°C, the rates of cellulose hydrolysis and glucose degradation are approximately equal, and yields in a batch reaction are very low. As temperature is increased, the rate of hydrolysis increases faster than that for sugar degradation, and at 240°C-265°C the rate of hydrolysis is approximately three times greater than the rate of glucose degradation. This tradeoff between rates of cellulose hydrolysis and sugar degradation leads to higher yields as temperature is increased provided the reaction time is reduced, as shown in Figures 2 and 3.

Concentrated acid breaks the hydrogen bonds between adjacent cellulose chains, rendering the structure amorphous and readily hydrolyzed at low temperatures where sugar degradation is not a problem. The decrystallization and hydrolysis of cellulose may be accomplished at approximately ambient temperature by the use of concentrated acids such as hydrochloric, sulfuric, and hydrofluoric acids. In all of these processes, the cellulose feedstock is dried and treated with concentrated acid to decrystallize the cellulose which is then is hydrolyzed with water at moderate temperatures to form simple sugars. All concentrated acid hydrolysis processes are capable of yields that approach 100%.

Acid Hydrolysis Options

Description of the Overall Process. The overall process, for converting cellulosic feedstocks into ethanol is summarized in Figure 4. The feedstock is first chipped, shredded, or milled to the size appropriate for the process. This material is then fed to the hydrolysis step in which the hemicellulose, amorphous cellulose, and crystalline cellulose are decomposed into their component sugars, according to the kinetics outlined above. Solids left after hydrolysis are generally separated from the liquid stream and burned to produce steam for heat or power generation. The soluble sugar stream is neutralized with calcium hydroxide, and the calcium sulfate formed is filtered out for waste disposal. The neutralized sugar stream is fermented into ethanol, with carbon dioxide formed as a by-product. The ethanol is concentrated to 94 percent by weight in the overhead stream of a distillation column, while the bulk of the water and stillage (left over sugar) from the bottom of the distillation column is disposed of. Finally, the overhead ethanol is sent to a dehydration column to break the azeotrope and produce anhydrous ethanol product for fuel use.

The decomposition of the cellulose in biomass can be catalyzed by a number of acids such as hydrochloric, hydrofluoric, and sulfuric acids. Although the overall process can be conveniently visualized as shown in Figure 4, the actual processes vary considerably to most fully capitalize on the acid properties while addressing key economic requirements. In this section, the principle features of several acid hydrolysis options that have been considered by the program are briefly summarized.

High Temperature, Dilute Acid Plug Flow Reactor. At high temperatures
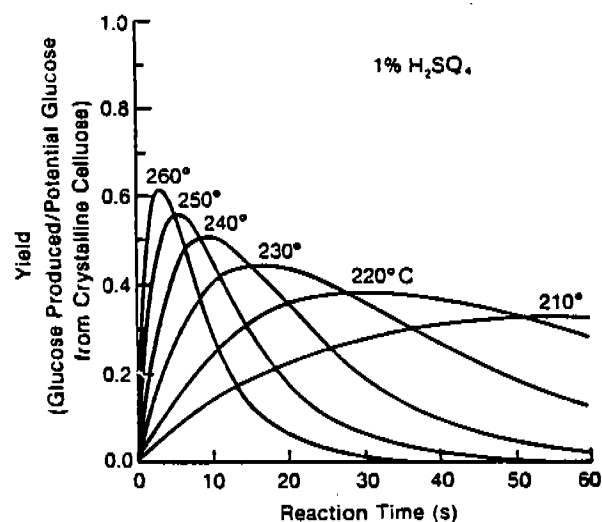
SULFURIC ACID HYDROLYSIS

Figure 2. Glucose Yield from the Hydrolysis of Crystalline Cellulose as a Function of Reaction Time and Temperature.
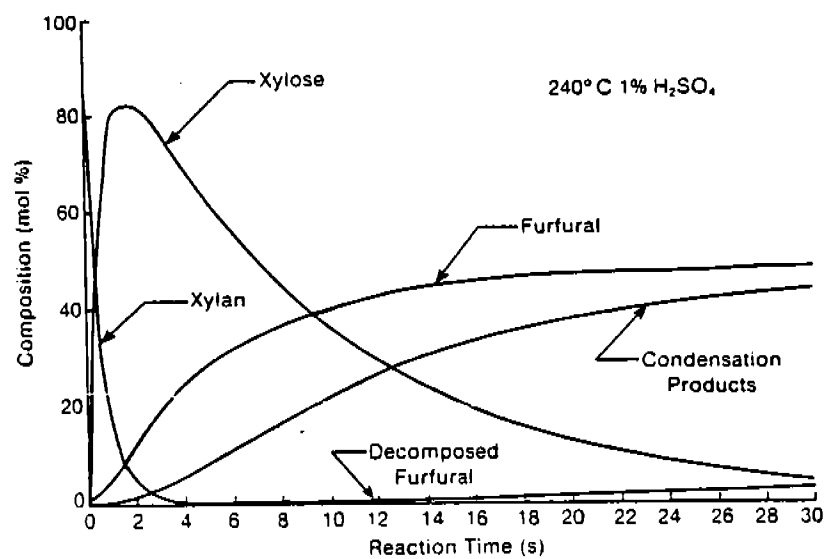

Figure 3. Plot of Yield vs Time for Species Involved in Xylan Hydrolysis.
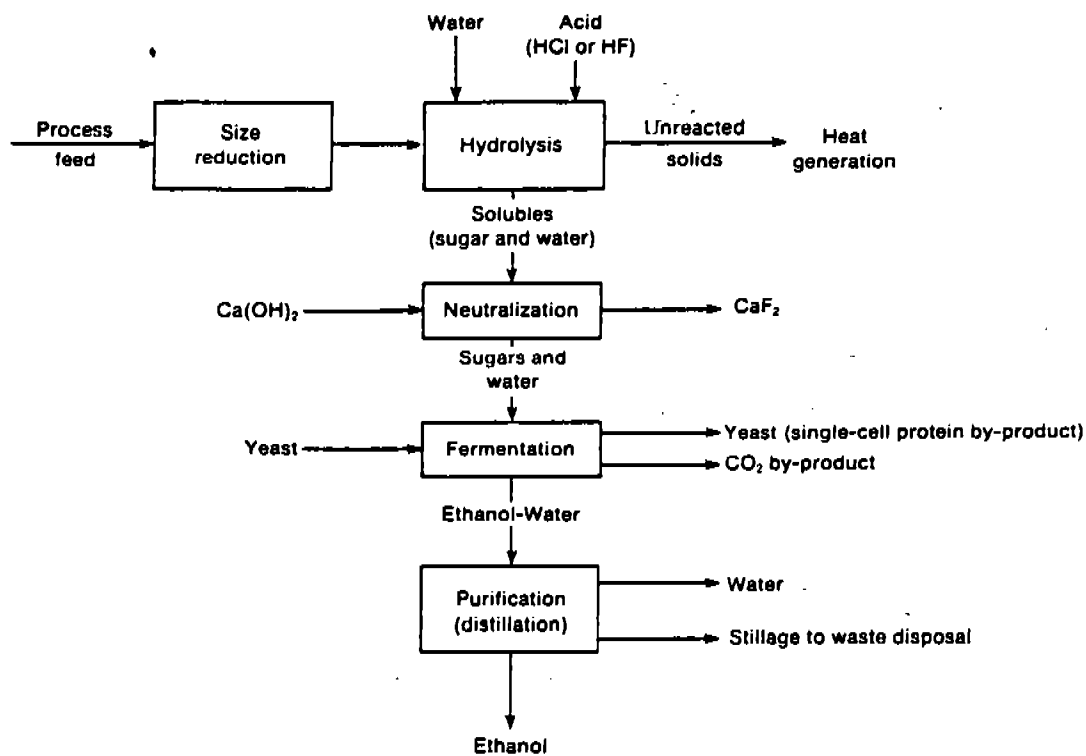
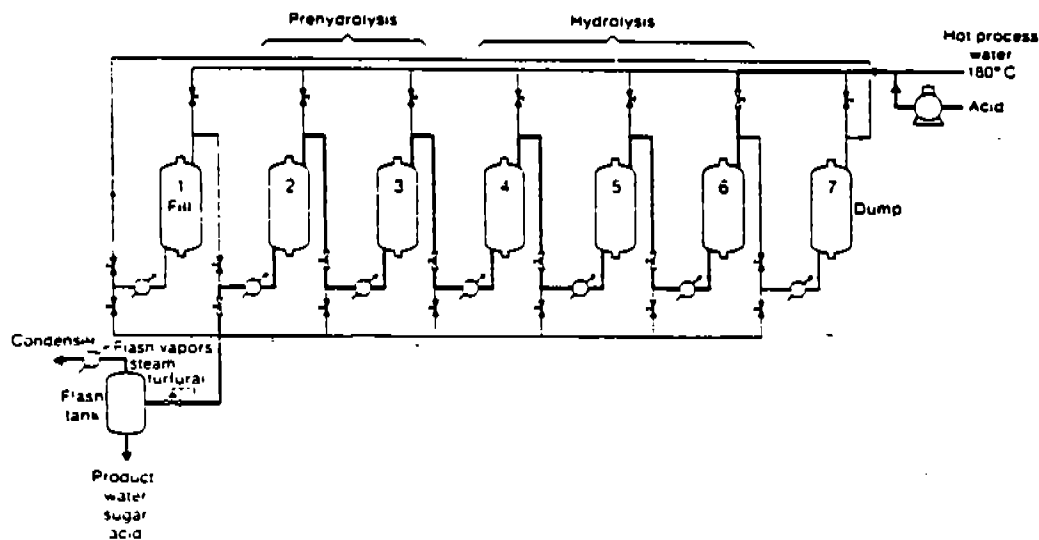Figure 4. Cellulose-to-Ethanol Overall Acid Hydrolysis Processing Plan.

Figure 5. Progressing Batch Reactor Schematic

(265°C, 1% H_2SO_4), the rate of hydrolysis is three times faster than the rate of glucose degradation (Kwarteng 1983), and at short residence times (four seconds), the glucose yield is 55%, while xylose is degraded into furfural with a yield of 67%. The plug flow reactor is designed to process wood slurries at high temperatures for very short residence times to maximize cellulose hydrolysis while minimizing sugar degradation. This process has been run for approximately 10 years at the bench scale at Dartmouth University in a 1/4 inch diameter reactor, with low solids concentrations (10%) at the pump inlet, primarily for gathering kinetic data (Grethlein 1982), and tests at Dartmouth University confirmed that a 20% solids slurry could be pumped after prehydrolysis. A pilot scale reactor (200 lb solids/hr) of similar design has been operated at SERI for two years (Hoagland 1986, Wright 1983) with results similar to those obtained at Dartmouth. The reactor has been modified to test the pumping of prehydrolyzed slurries, but the feasibility of extended operation on prehydrolyzed feedstock must still be demonstrated. Furthermore, the rate and efficiency of the fermentation must be determined. Because of the amount of degradation products produced, the cost and performance of the clean up system is a major uncertainty.

Percolation Dilute Acid Hydrolysis Reactor. Percolation reactor technology was first developed in Germany in the late 1920's (Wenzl 1970). During the 1940's, an improved percolation process known as the Madison process, was developed in the United States (Harris et al 1945, Gilbert et al 1952). The percolation reactor technology is currently the basis of an industry in Russia with approximately 40 commercial plants. Yields of 60% and total sugar concentrations of 4% are typically reported. Pilot scale studies have also been conducted in Brazil (Carvalho et al 1983), New Zealand (Burton 1982, Mackie 1982) and Austria (NRCC 1983). This process passes water containing dilute acid through a bed of chips. In this manner, the solid biomass is held long enough to release its sugars even at moderate temperatures (~180°C) while the sugar is removed with the water before it can degrade significantly. By increasing the water throughput, higher sugar yields are possible, although at the expense of a more dilute sugar stream. Thus, one must consider the tradeoff between sugar yield and concentration.

Progressing Batch Reactor. A countercurrent reactor configuration offers considerable advantages over percolation. The rate of sugar production is greatest when the solids are first introduced into the reactor. With countercurrent flow of solids and liquids through the reactor, the liquids outlet is adjacent to the solids inlet. Thus, the largest fraction of sugars has only a small distance to travel before it is washed out of the reactor, minimizing the time available for sugar degradation and maximizing the yield and sugar concentration. For similar reaction conditions, the yield is calculated to increase from approximately 60% to 80% and sugar concentration increased by 20% (Song and Lee 1982).

The continuous countercurrent reactor is attractive on paper, but, the movement of a concentrated stream of biomass and water into and out of a pressurized reactor is a very complicated operation, even when the solids and liquids are moving in the same direction (as in a plug flow reactor). The progressing batch hydrolysis process uses several percolation reactors in series to simulate countercurrent flow of liquids and solids. In this way, the advantages of countercurrent flow are potentially achieved, and the mechanical and operational simplicity of the percolation reactor (all solids

handling is done at atmospheric pressure) is retained (Wright et al 1985). Figure 5 shows several percolation reactors in series. The liquid enters reactor 6, flows from right to left and exits from reactor 2. Hydrolyzate is flashed to quench the hydrolysis and degradation reactions.

After 15-30 minutes, the reactors are cycled by simple changes in valve position. Fresh liquids enter reactor 5, and exit from reactor 1. Reactor 7 is filled with fresh wood and the residual solids in reactor 6 are discharged. The net effect is that fresh solids have entered the reactor train at the left and spent solids are discharged after leaving the last hydrolysis reactor in the train on the right. The first reactor in the series is used as a prehydrolysis reactor, while the remaining four reactors are used as hydrolysis reactors. Thus, both amorphous and crystalline sugars can be recovered with high efficiencies. The use of extensive heat recovery results in a very low energy usage.

<u>Low Temperature Concentrated Sulfuric Acid Hydrolysis</u>. The low temperature, concentrated sulfuric acid hydrolysis process operates on the principle that the concentrated acid will break down the hydrogen bonds between adjacent crystalline cellulose chains, rendering the cellulose amorphous and easily hydrolyzed at conditions where sugar degradation is slow and yields are high. By using low cost sulfuric acid, the large capital investment and energy consumption required for acid recovery can be eliminated. Such processes have been studied at the pilot scale in Japan (Wenzl 1970), by the USDA Northern Regional Research Laboratory in Peoria, Illinois (Dunning and Lathrop 1945), by Purdue University (Tsao et al 1982), and by the Tennessee Valley Authority (Barrier 1985).

The wood is mixed with a recycled solution of sulfuric acid and sugars (primarily glucose) and conveyed to the prehydrolysis tank where they are heated to 100°C and held for two hours while the hemicellulose is hydrolyzed with 7% acid and a yield of 90%. After the prehydrolysis, the sugars produced are removed by what is essentially a countercurrent leaching carried out in progressing batch fashion, and then centrifuged to remove much of the remaining water. The solids are slurried with water and acid and pumped to a tank, where they soak for two hours to allow the acid time to permeate uniformly into the fibers. The loading is 0.25 lb of sulfuric acid per pound of dry solids, and the temperature is kept low to prevent significant hydrolysis from occurring. The slurry is centrifuged, and the liquid stream recycled.

The acid impregnated solids are sent to the rotary dryers and dried to approximately 10% moisture at 85°C. This operation has high capital and operating costs. The drying removes water but not the sulfuric acid, concentrating the acid to 83%. Concentrated acid disrupts the lattice of crystalline cellulose by breaking the hydrogen bonds between adjacent cellulose chains. The dry acid-impregnated solids are then mixed with water and heated to 140°C with steam. Now the cellulose can be hydrolyzed to glucose in a few minutes at low temperature, with minimal formation of by-products. The yield of glucose from cellulose is approximately 80% of theoretical. The processing steps following the dryer are relatively fast and are performed in a continuous manner.

The product from the hydrolysis reactor is discharged to a flash drum, and the solids and liquids are separated in a centrifuge. The liquid stream

(consisting of water, sugars, and acid) is recycled to prehydrolysis, while the solids are burned to provide the energy for the process. The sugars produced in both the hydrolysis and hemicellulose hydrolysis reactors are removed in the leaching process following prehydrolysis. This product stream has a composition of 7.0 wt % glucose and 5.5 wt % xylose (Wright and d'Agincourt 1984).

Liquid Phase Concentrated Hydrochloric Acid Processing. The liquid phase concentrated HCl hydrolysis system uses a solution of 40% HCl to decrystallize the hydrolyze lignocellulosic materials with a yield of essentially 100% (Goldstein et al 1983). Because HCl is an expensive acid, an HCl recovery system must be used. This process has been studied extensively, and a plant has been operated in Germany since 1925 (Bergius 1937, Rheim 1980).

The incoming wood is dried to 10% moisture. The hydrolysis system uses six replicate rubber lined reactor vessels to provide countercurrent flow of wood chips and hydrochloric acid. The acid stream is fed to the reactors at a concentration of 41%; it decreases in acid concentration and increases in sugar concentration as it progresses through the four reactors. The reactor residue is washed with water and with 30% acid to recover residual acid in the remaining lignin. The lignin is discharged from the fifth reactor, dried, and burned. The hydrolysis reaction residence time is 1 hour at 35°C, and the operating pressure is slightly above atmospheric to keep air out. There is no prehydrolysis step because sugar degradation is negligible, and the cellulose and hemicellulose are hydrolyzed with essentially 100% efficiency to simple sugars and sugar oligomers.

The solution of acid and sugars is pumped to the evaporators where 95% of the HCl fed to the reactors is taken overhead in two stages with water vapor, separating it from the crude water solution of sugars and lignin. The combined stream is approximately 30% HCl in water, which is then fed to the acid reconcentration system. The acid reconcentration process, designed to upgrade 30% hydrochloric acid to 40%-41% HCl, utilizes two columns. The columns operate at different pressures to shift the concentration of the azeotrope and take advantage of this shift to remove water. The process energy required is only the net requirement to remove the water by evaporation from the gross feed stream. The system is constructed of glass-lined steel with ceramic packing and includes corrosion-resistant heat exchangers and a vacuum pump. Makeup acid is added in an atmospheric pressure adsorption system. The post hydrolysis system is designed to hold the crude product stream at 100°F for about 1 hour in the presence of a few percent HCl to break down the polysaccharides formed in the main hydrolysis to monomeric glucose and xylose. Approximately 90% of the potential sugars can be fermented (Wright and Power 1985).

Liquid Phase Hydrofluoric Acid. Like all concentrated acid processes, the liquid phase HF process has yields approaching 100%. Even so, the capital and energy requirements of the hydrolysis are large. Also, losses of HF from the process must be absolutely zero, first because HF is an expensive acid ($0.66/lb) but primarily because of its extraordinarily hazardous nature (Wright and Power 1985).

Liquid phase HF processes have been studied only at the bench scale. Work has been carried out in Germany (Fredenhagen 1933), Denmark, and France

(Bentsen 1983, Defaye 1981), and at Michigan State University in the United States (Selke et al 1983). In recent years, a gas phase HF process has also been investigated at Hoechst AG in Germany (Franz et al 1983) and in Canada (Ostrovski et al 1984). This report deals only with liquid phase processes, as little performance information has been released on the gas phase options.

The first step in the hydrolysis section is to dry the incoming wood chips to 5% moisture to give the highest yield (near 100%). Close control over the moisture content out of the dryers is a necessity. Any moisture entering with the wood chips that is not consumed in the hydrolysis reaction will leave the reaction as a water/HF azeotrope (approximately 2 parts water to 1 part HF). The cost of HF lost in this manner increases very sharply with even small amounts of excess water in the feed. To eliminate the loss of HF from the process, the water content of the incoming feed should be reduced to 3%. Due to the difficulty of completely drying the wood chips, we assume that the feed is dried to 5% moisture.

The dried wood chips are sent to the hydrolysis reactor bank where they are contacted with HF at 23°C. The ratio of HF to wood is 2.7/1 by weight. The reaction products are sent to the acid recovery section, while the sugars are repeatedly heated and flashed to vaporize the HF and water. The bottom stream from the final flash tank is an HF-free stream of solid crystalline sugar and lignin. The flash vapors--HF and water--are sent to a distillation column, where water is removed and the HF recycled. Water is added to the sugars and lignin, and the lignin is removed by filtration. The sugar stream from the filter (containing both monomeric and oligomeric sugars) is heated and sent to the posthydrolysis reactor where the oligomeric sugars are converted into monomeric sugars. The overall hydrolysis efficiency is 90%. The monomeric sugars are then sent to neutralization and fermentation. A major piece of auxiliary equipment is the refrigeration system, required to remove the large exothermic heat of reaction from the hydrolysis reactor and to cool the distillation column condenser.

Summary of Acid Hydrolysis Economics

With so many options presented, plus others not discussed, for acid hydrolysis of lignocellulosics to ethanol, the choices must be narrowed to a few for focused development if the program is to make reasonable progress. In addition, the economic potential of each must be judged to decide which, if any, have sufficient economic merit to warrant research and development. Therefore, process engineering studies have been completed on the acid hydrolysis processes presented. In these studies, processes were designed based on descriptions available from the literature or from other relevant information, and improvements made where possible to conform with current technology. Material and energy balances were then calculated for each process configuration, and equipment sizes were estimated. From this information, capital and operating costs could be developed based on established procedures such as the ICARUS capital cost estimating program. Finally, the process was reviewed to determine whether technology improvements appeared possible and the impact on process economics was estimated. This procedure allowed us to develop a base case and improved case scenario for each option.

Table 1 provides a breakdown of the energy consumption by process area for the acid hydrolysis options discussed, while Table 2 summarizes the capital

Table 1. Energy Consumption by Process Area for Lignocellulose to Ethanol Facilities with Various Hydrolysis Processes

	Plug Flow		Progressing Batch		Concentrated H_2SO_4		Liquid HCl		Liquid HF	
	Electrical	Steam	Electrical	Steam	Electrical	Steam	Electrical	Steam	Electrical	Steam
Section	0.5	1.9	0.4	1.4	0.3	1.2	0.3	1.3	0.3	1.1
Feed	32.2	243.6	3.1	77.6	6.0	124.7	4.5	665.1	2.4	388.9
Hydrolysis	2.1	5.3	2.6	6.6	2.5	6.2	1.0	2.6	1.0	2.5
Fermentation	10.0	44.0	12.5	55.4	11.8	52.1	4.7	20.8	4.6	20.2
Distillation	0.2	53.8	0.1	14.2	0.0	0.0	0.0	0.0	0.0	0.0
Furfural Recovery	0.8	0.0	0.6	0.0	0.5	0.0	0.5	0.0	0.5	0.0
Offsite Tank	0.5	164.0	0.7	207.9	0.6	194.9	0.2	74.9	0.2	72.3
Environment	17.0	11.0	13.2	8.5	11.3	7.3	13.9	9.0	11.0	7.1
Utilities	4.0	11.0	4.0	11.0	4.0	11.0	4.0	11.0	4.0	11.0
	67.3	534.6	37.2	382.6	37.0	397.4	29.2	784.7	23.9	503.2

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Table 2. Capital Cost by Process Area for Lignocellulose to Ethanol Facilities with Various Hydrolysis Processes

Section	Plug Flow	Plug Flow*	Progressing Batch	Concentrated H_2SO_4	Liquid HCl	Liquid HF
Feed Handling	8.5	8.5	6.7	6.0	6.1	5.6
Hydrolysis	25.7	25.7	15.0	43.8	53.9	34.1
Fermentation	8.1	8.1	9.3	8.9	5.3	5.2
Distillation	13.0	13.0	14.9	14.3	8.3	8.1
Furfural Recovery or Concentration	5.5	5.5	2.5	0.0	0.0	0.0
Offsite Tankage	5.1	5.1	4.4	3.9	4.1	3.9
Environmental	10.9	11.1	12.6	12.1	6.3	6.7
Utilities	39.5	43.3	32.3	33.4	35.8	31.8
	116.2	120.2	97.3	122.5	120.3	95.3

*Furfural concentrated and burned to produce steam and electricity.

Table 3. Cost of production summary for lignocellulose-to-ethanol facilities with various hydrolysis processes (25,000,000 gal/yr, mixed hardwood at $42/ton).

	Cost of Production (¢/gal Ethanol)					
	Plug Flow	Plug Flow*	Progressing Batch	Concentrated H_2SO_4	Liquid HCl	Liquid HF
Raw materials						
Wood	104.6	104.6	77.5	68.2	69.9	62.1
Acid	6.5	6.5	6.5	17.4	11.9	39.9
Lime	3.5	3.5	3.5	9.4	1.6	0.7
Chemicals	3.5	3.5	2.6	2.3	2.3	2.1
Utilities						
Water	0.9	0.9	1.1	1.3	0.9	0.5
Steam	0.0	0.0	0.0	0.0	35.2	2.7
Labor	7.2	7.1	6.0	7.6	7.4	5.9
Overhead & maintenance	34.0	33.7	28.6	35.9	35.3	27.9
Byproducts						
Furfural	-70.5	0.0	-3.2	0.0	0.0	0.0
Electricity	-20.8	-31.0	-23.8	-21.8	22.3	-17.6
Annual operating cost	68.8	128.8	98.8	104.7	139.6	126.1
Capital charges (FCR=0.13)	60.0	59.4	50.3	63.2	62.1	49.2
Ethanol selling price	128.8	188.2	149.1	182.4	201.8	175.2

*Furfural concentrated and burned for energy production.

costs for each process. The cost of production of ethanol is presented in Table 3 for each process. Although space constraints prevent a detailed discussion of the results, Wright (1986) provides more information on the process evaluations.

From these studies, the following conclusions are drawn. The high yields enjoyed by the concentrated acid processes do not overcome the penalties imposed by the use of large quantities of acid. In the concentrated sulfuric acid process, these liabilities include high capital cost and high acid consumption, while the halogen acid processes suffer from extreme complexity, high capital and operating costs involved in the recovery and recycling of the expensive halogen acids, the high costs associated with the loss of even small amounts of expensive acid, and the less readily quantifiable disadvantages of working with highly toxic substances.

The progressing batch hydrolysis concept is projected to be superior to the plug flow and halogen acid hydrolysis concepts if the objective is to produce ethanol and electricity. The progressing batch hydrolysis system produces sugars with higher yields than the plug flow reactor, requires less capital investment and energy, and is an inherently simple and proven mechanical design. These advantages carry over into systems with five carbon sugar fermentations as the progressing batch reactor appears to be an inherently efficient producer of five carbon sugars. The major need in this process is for operating data on progressing batch operation to determine the actual performance of the process and establish whether it matches that assumed for this analysis.

In the near term, the co-production of furfural by the plug flow reactor is a significant advantage enjoyed by no other hydrolysis process. Large quantities of a high value byproduct from waste xylose are produced with only a modest additional requirement for capital or energy. This should allow furfural to be sold as a byproduct at a fraction of its current selling price, facilitating expansion into readily identifiable, and in many cases, commercially proven markets and processes. However, this advantage would be limited by the market for furfural which is much less than that possible for ethanol as a fuel.

The concentrated sulfuric acid process has a long history of development. There is little room for improvement in the yield, while the acid consumption costs of the process are inherent to the design considered. Recovering sulfuric acid from the product stream for less than its extremely low cost (3.25 /lb) will be difficult. This is a relatively safe reactor design in that there are no major technical barriers to its working.

The liquid phase HCl process is commercially proven and has a long history of development. As long as a thermal method is used for the recovery of the acid, this process will not be able to compete. The capital and energy costs involved in acid recovery are immense due to the large volume of liquid that is cycled and the exotic materials of construction. Several investigators have proposed using either solvent extraction or membrane processes to recover the hydrochloric acid. The capital cost reductions indicated for the electrodialysis process are not large enough to significantly change the economics. No conclusion as to the value of the solvent extraction process can be drawn without a careful analysis. A useful observation, however, is that in general

industry is moving away from the use of concentrated acid processes wherever possible. The maintenance and operation difficulties involved in such processes are large enough that even where they are profitable, alternatives are actively sought.

Acid Hydrolysis Research

Since resources are limited, the program has focused on development of the most promising acid hydrolysis processes that were identified by studies such as these plus others on options such as the percolation reactor or gaseous HCl hydrolysis. The plug flow reactor is under development at SERI since it has significant near-term potential for producing both ethanol and the by-product furfural. A two-stage process that employs a prehydrolysis vessel followed by the plug flow reactor is currently being studied for processing of 18 to 20% solids concentrations deemed necessary for commercial feasibility, although delays have been encountered in the operation of the process. A private firm has recently contracted with SERI to obtain operational data on the unit that will be used to evaluate its commercial potential as well as for design of a commercial process, if promising. Research is also in progress by TVA to establish conditions for fermentation of the product hydrolyzates from the plug flow reactor to ethanol.

The progressing batch reactor has the potential of achieving higher sugar yields at reasonable concentrations than the plug flow reactor. Furthermore, its economics are not dependent on sale of a by-product with a limited market such as furfural, although an electricity credit is still important. However, since significant uncertainties remain in how closely the performance of the progressing batch reactor will approach predictions based on countercurrent flow, tests are now underway to evaluate its performance. Operation of a single stage percolation reactor has been completed to establish base line data for comparison with the progressing batch system and to establish hardware design. A two-stage system has been built and will be operated to estimate the benefits of staged operations. The results from these tests will be used in conjunction with a modeling study to estimate the performance of a multistage process, and the total system will be evaluated if the model predictions and two-stage operation demonstrate sufficient merit. A study is being initiated at Brown University to understand the hydrodynamics of the progressing batch reactor to insure proper liquid distribution throughout the bed.

The Tennessee Valley Authority is developing a concentrated sulfuric acid process, and DOE/SERI is cofunding some of this research. The focus of this effort is on developing inexpensive acid recovery processes since the economics are very sensitive to acid loses. Thus, the University of Arkansas, University of Missouri at Rolla, and Purdue University are all under subcontract to TVA to develop low cost acid recovery systems.

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DILUTE ACID HYDROLYSIS OF HIGH SOLIDS WOOD SLURRIES IN A TWO-STAGE CONTINUOUS FLOW PROCESS

A. Brennan, D. Schell, W. Hoagland, P. Werdene
Solar Energy Research Institute
1617 Cole Blvd.
Golden, CO

ABSTRACT

Research in SERI's Biotechnology Branch has addressed the technical feasibility of pumping high-solids wood slurries (>18%) in a continuous two-stage acid hydrolysis process. The research was intended to resolve a primary uncertainty in the potential of the technology to produce fermentable sugars for fuel-grade ethanol. The results of this research are described in the attached report.

The approach of the experiments was to prehydrolyze the wood at mild conditions prior to the hydrolysis reactor, thereby degrading the hemicellulose. The resultant prehydrolyzate slurry resists the plugging, dewatering and bridging typical of water-wood mixtures and can be pumped more easily at relatively high concentrations (>18%).

The SERI experiments encountered several major equipment problems that delayed progress. Problems with the automatic wood feeder and the airlock hopper were resolved, but problems with the Moyno progressing cavity pump remain. The pump problems prevented sufficient operation to demonstrate pumpability of the high solids slurries. However, we believe that some limited additional testing with a new Moyno pump would provide sufficient data to successfully demonstrate the process. Currently, work is being continued with funding by a private company that is interested in commercializing the process for the production of specialty chemicals.